

Thermodynamic regulation of electrolyte to achieve air-tolerant viologen-based flow battery

Mingbao Huang^a, Wenjin Li^a, Dehan Lin^a, Kai Wan^a, Zhiyong Fu^a, Zhipeng Xiang^{a,*}, Zhenxing Liang^{a,b,*}

^a Guangdong Provincial Key Laboratory of Fuel Cell Technology, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510641, PR China

^b State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510641, PR China

ARTICLE INFO

Keywords:

Redox flow battery
Viologen-based anolyte
Host-guest assembly
Air tolerance
Cyclability

ABSTRACT

Aqueous organic redox flow battery (AORFB) is one promising grid-scale energy storage technology. However, the application is seriously hindered as AORFB cannot be stably operated in air, and the reason lies in the poor air tolerance of electroactive organics. Herein, we develop a thermodynamic regulation strategy through host-guest assembly to improve the air tolerance of the viologen-based anolyte. It is found that the reduced state of viologen forms a host-guest complex with the hydroxyethyl- β -cyclodextrin (HE- β -CD) molecule via hydrophobic effect, and the host HE- β -CD serves as a steric hindrance to kinetically shield the reduced viologen against oxygen attack. As demonstration, a flow battery fed with the viologen/HE- β -CD anolyte achieves a high Coulombic efficiency ($\sim 99.9\%$) and superior cyclability ($\sim 97.73\%$ capacity retention rate over 300 cycles) when operated in air. This work provides a facile supramolecular method to tackle the most urgent issue of AORFB, which paves the way for its practical application.

1. Introduction

Flow battery can decouple the energy and power in principle, which enables its intrinsic safety, high efficiency and flexible application [1–6]. Electroactive organic molecules [7–11] have been explored to develop the transition metal-independent aqueous organic redox flow battery (AORFB). Among them, viologen derivatives feature decent solubility, high reversibility, and near-neutral operation, which have shown a superior performance in AORFB [12–14]. However, it is notable that a glove-box filled with inert gas is required as air threatens its stable operation [15,16], which is understandable as follows. Thermodynamically, oxygen in air can oxidize the charged state of the active species in anolyte (e.g. -0.45 V vs. SHE for methyl viologen [12]), thereby leading to a serious capacity fading. Kinetically, the highly active intermediate (like viologen radicals) yields a high reaction rate with oxygen ($k > 10^6 \text{ M}^{-1} \text{ s}^{-1}$) [17]. Oxygen reduction reaction mediated by the reduced-state species occurs during the discharge/charge course (Scheme 1) and, thus, triggers a dramatic change in the electrolyte pH, which is harmful to the chemical stability of viologen molecules [18,19]. Therefore, it is urgent

to develop air-tolerant strategies for the practical application of AORFBs.

The elevation of the redox potential can thermodynamically weaken the driving force for the oxidation and improve the oxygen tolerance [20]. For example, by grafting electron-withdrawing ester group onto 2-site of viologen skeleton, the redox potential of viologen is positively shifted to 0.47 V vs. SHE, enabling an excellent radicals' stability over 40 h in air [21]. Stoddart *et al.* [22] also reported air-stable bisradicals $\text{mHo}[2]\text{C}^{2+6+}$ with sufficiently positive redox potentials ($E_{\text{ox}1} = 0.54$ V, $E_{\text{ox}2} = 0.85$ V). Such potential-elevating strategies are, however, infeasible when viologen derivatives are used as the anolyte in flow battery. Alternatively, kinetic strategy seems more appealing to improve the radicals' stability without sacrificing the thermodynamic potential. Steric hindrance has been employed to spatially prevent the organic radicals from the side reactions [23–28], which can be realized by a facile non-covalent interaction method [20]. For example, the guest azafullerenyl radical $\text{C59N}^{\bullet}$ could be assembled in the host [10]cycloparaphenylene, and the σ -dimerization was substantially mitigated by the shielding effect [23]. Our previous work demonstrated that the

* Corresponding authors at: Guangdong Provincial Key Laboratory of Fuel Cell Technology, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510641, PR China.

E-mail addresses: xzp20209094@scut.edu.cn (Z. Xiang), zliang@scut.edu.cn (Z. Liang).

<https://doi.org/10.1016/j.ensm.2024.103267>

Received 28 September 2023; Received in revised form 8 February 2024; Accepted 13 February 2024

Available online 15 February 2024

2405-8297/© 2024 Elsevier B.V. All rights reserved.

introduction of a host hydroxyethyl- β -cyclodextrin (HE- β -CD) could stabilize the two-electron reduced viologen against the proton attack [25]. These findings inspire one to address the oxygen-tolerant issue by supramolecular chemistry strategy.

A home-made viologen derivative, 1,1'-bis[3-(trimethylammonium)propyl]-4,4'-(2,5-thiophenediyl) bipyridinium tetrabromide [(ATBPy)Br₄, Fig. S1] [29], is used as the anolyte. Its air tolerance is achieved by forming a host-guest assembly with HE- β -CD and, the air-stable (ATBPy)Br₄-based all-organic flow battery is demonstrated for the first time. The mechanism of the air tolerance is understood as follows. Scheme 1 presents the assembling process of the host-guest complex, in which the doubly reduced (ATBPy)²⁺ is sandwiched between two HE- β -CD by the hydrophobic effect. As such, the reduced molecule is well spatially shielded by the host HE- β -CD against the oxygen attack. As demonstration, the flow battery can realize a high Coulombic efficiency (CE) of ca. 98 % when the (ATBPy)Br₄ anolyte is fully exposed to air. A simple packaging can further increase the CE to 99.9 %, which is comparable to that in an inert atmosphere.

2. Materials and methods

2.1. Synthesis

The compounds of 1,1'-bis[3-(trimethylammonium)propyl]-4,4'-(2,5-thiophenediyl) bipyridinium tetrabromide and (ferrocenylmethyl)trimethylammonium chloride were synthesized following previous literatures (see Supplementary material).

2.2. Electrochemical characterization

A CHI730E (Shanghai, China) electrochemical workstation was used to collect the cyclic voltammogram (CV) with a standard three-electrode setup, including glassy carbon (diameter of 3.0 mm) working electrode, Ag/AgCl reference electrode and platinum counter electrode. CVs were recorded at two different scan rates of 10 and 100 mV s⁻¹ with 4.0 mM active material dissolved in 0.50 M KCl_{aq} solution. Differential pulse voltammetry (DPV) was used to determine the transfer electron number of electro-active component (4.0 mM, with different equiv. HE- β -CD) with an amplitude of 0.05 V and a pulse width of 0.06 s. Linear sweep voltammetry (LSV) was used to collect the limiting current of electro-active component (1.0 mM, with different equiv. HE- β -CD) at different states (oxidized and reduced states) by using the gold disk ultramicroelectrode with a scan rate of 25 mV s⁻¹. The diffusion coefficient

(D) can thus be obtained according to a steady-state current equation as follows:

$$i_{ss} = 4nFDC_0r \quad (1)$$

where i_{ss} represents the steady-state current (A), n is the electron transfer number (= 2), F is the Faraday constant (= 96,485 C mol⁻¹), D has been defined as above (cm² s⁻¹), C_0 is the bulk concentration of (ATBPy)Br₄ (= 1.0 mM), and r is the radius of the gold disk ultramicroelectrode (= 15.0 μ m).

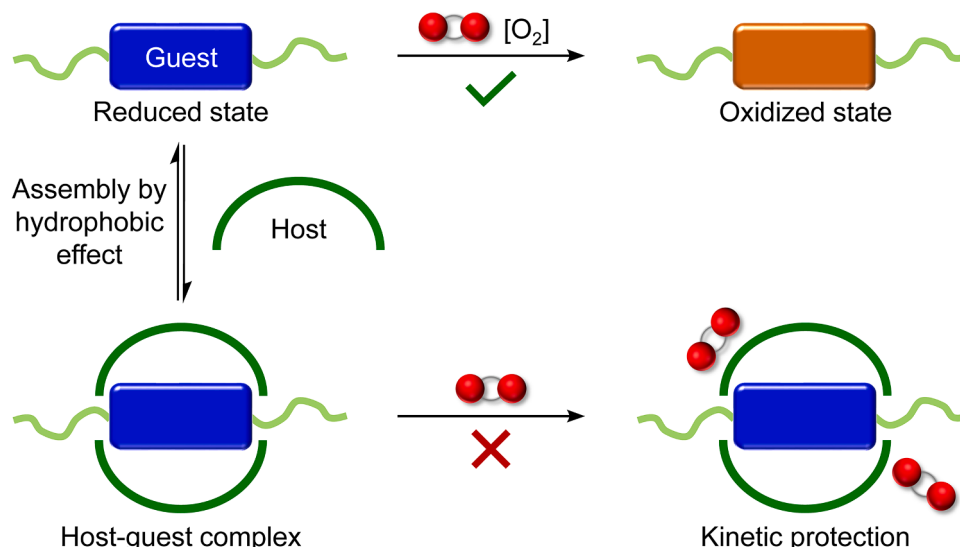
2.3. Flow battery test

A laboratory-scale flow battery consisting of titanium collector plate, porous graphite felt electrode (3.0 cm $\times$ 3.0 cm in size, 4.0 mm thickness) and commercial DSVN anion-exchange membrane (AGC seleminion) was assembled. With adding KCl (2.0 M) as the supportive electrolyte, 5.0 mL 0.10 M (ATBPy)Br₄ anolyte and 25.0 mL 0.10 M FcNCl catholyte were circulated by a peristaltic pump (Longer BT100-2 J) at a flow rate of 60 mL min⁻¹. The flow battery was operated in either air or an argon-filled (99.999 % Ar) glovebox (Universal 2440/750/900), and the performance was collected on a battery test system (Neware BTS 3000) with a range of 5 V and 6 A. The operating conditions are given in Table S1.

3. Results and discussion

3.1. Host-guest complex structure

The doubly-reduced structure of (ATBPy)²⁺ and the interaction with cyclodextrin are explored by the ¹H nuclear magnetic resonance (NMR) spectroscopy, as shown in Figs. S2 and 1a. Herein, a well-defined-structure β -CD (inner surface: H₃ and H₅; exterior rim: H₂, H₁, H₄ and H₆, see Fig. S3a) is used for the NMR test as the commercially available HE- β -CD has different isomeric structures and its NMR signals are too complicated to analyze (Fig. S4) [25]. It is seen that the doubly-reduced (ATBPy)²⁺ features polyene structure and yields a specific shift in the chemical shift of proton resonances after the introduction of β -CD. The “i” and “h” protons yield remarkable upfield shifts (0.19 and 0.08 ppm), indicating an increase of electron cloud density around them. It is, thus, inferred that the central core of (ATBPy)²⁺ should locate in the electron-rich inner cavity of β -CD [30]. The “e” and “f” protons show downfield shifts, which can be attributed to the electron-withdrawing effect of the hydroxy on β -CD terminals (Fig. S3b). Fig. 1b presents the two-dimensional nuclear overhauser enhancement (2D NOE)



Scheme 1. Steric hindrance of reduced-state viologen against oxygen attack by supramolecular chemistry strategy.

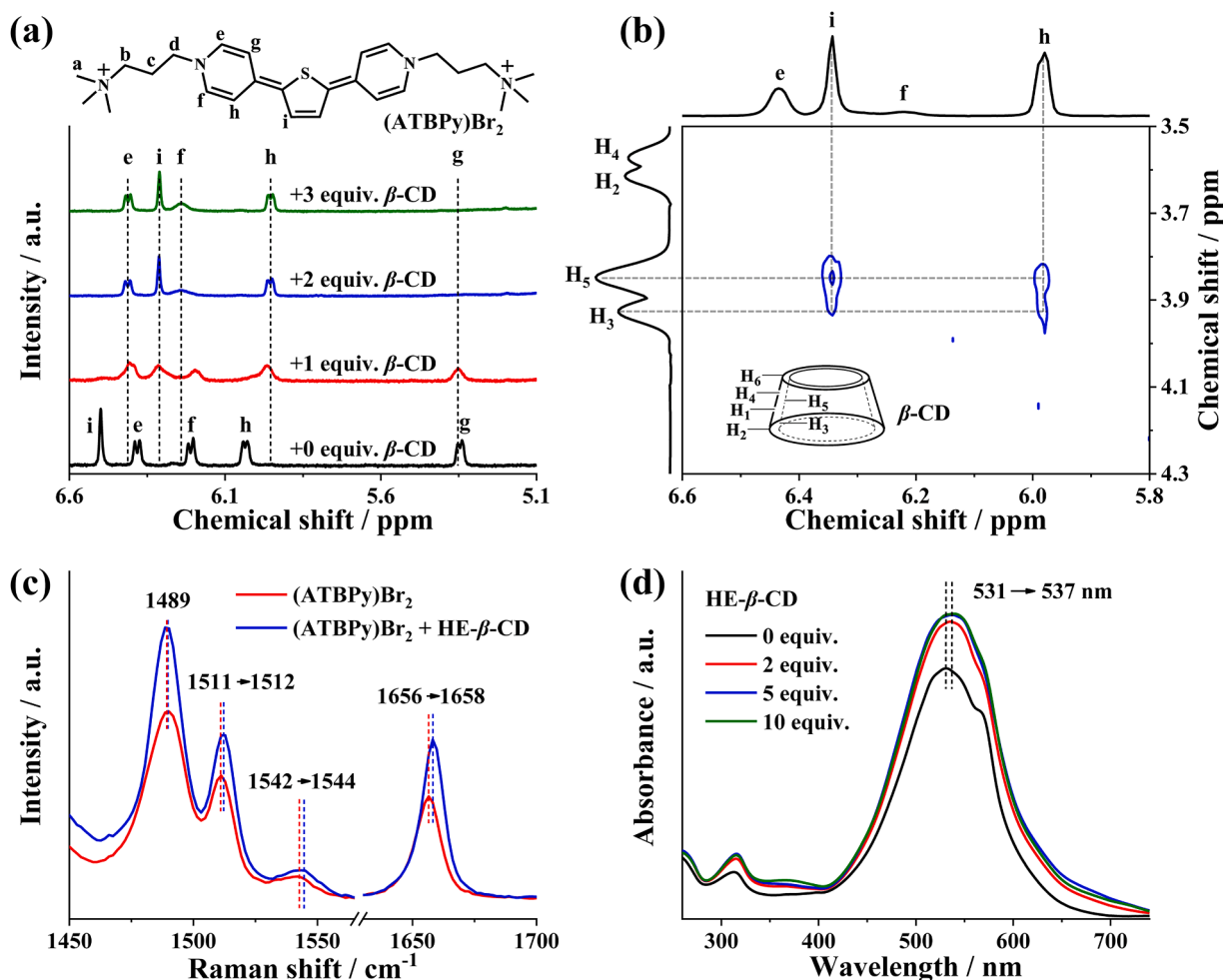


Fig. 1. (a) ^1H NMR spectra of (ATBPy) Br_2 with different equiv. (0, 1, 2, 3) β -CDs; (b) 2D NOE spectrum of (ATBPy) Br_2 with β -CD; (c) Raman spectra of (ATBPy) Br_2 and (ATBPy) Br_2 +HE- β -CD; (d) UV-vis spectra of (ATBPy) Br_2 with HE- β -CD.

spectroscopy. The presence of the two cross-peaks between “i, h” of (ATBPy) $^{2+}$ and “H₃, H₅” of β -CD strongly indicates that the two molecular segments are sufficiently close in space ($< 5 \text{ \AA}$) [31,32]. And such an interaction is understandable as the hydrophobic effect favours the supramolecular assembly between them. Therefore, it is concluded that as the guest, the hydrophobic polyene is included inside the host β -CD cavity, and the alkyl chain of hydrophilic quaternary ammonium is hanged outside of β -CD. Furthermore, it is noted that the chemical shift of (ATBPy) $^{2+}$ remains unchanged when an excessive amount of β -CD (> 2 equivalent) is added, indicating the formation of a ternary complex between them. That is, one (ATBPy) $^{2+}$ is encapsulated by two cyclodextrin molecules, as shown in Scheme 1 and Fig. S3c.

Considering the low solubility of β -CD, a highly water-soluble HE- β -CD is employed as the host for the practical application in AORFBs. The two cyclodextrin molecules have the same inner cavity, which are thus supposed to form similar assembly with the (ATBPy) $^{2+}$. Both Raman and ultraviolet-visible (UV-vis) spectra are used to study the proposed assembly structure and interaction. Fig. 1c shows four bands ranging from 1450 to 1700 cm^{-1} , being assigned as stretching vibration of C11=C12 (1489 cm^{-1}), symmetric and asymmetric stretching modes of C9=C10 (1511 and 1542 cm^{-1}), and stretching modes of C5=C7 and C6=C8 (1656 cm^{-1}) respectively, of polyene structure (Fig. S5). The bands are positively shifted in the presence of HE- β -CD, and the reason may be the formation of hydrogen bond between nitrogen site on the polyene skeleton and hydroxyl at the HE- β -CD terminals (Fig. S3b) [33]. The UV-vis spectra show that the absorption peak around 531 nm (π - π^* transition of the conjugated polyene structure [34]) yields a

bathochromic shift by 6 nm with the addition of 2 equiv. HE- β -CD (Fig. 1d). And further adding the HE- β -CD does not shift the absorption peak, indicating that one (ATBPy) $^{2+}$ molecule is assembled with two HE- β -CD molecules.

3.2. Electrochemical analysis

The electrochemical behavior is investigated by the cyclic voltammetry (CV). For the (ATBPy) Br_4 , the CV shows two single-electron-transfer redox peaks at -0.75 and -0.87 V (Figs. 2a and S6), which respectively correspond to (ATBPy) $^{4+}/(\text{ATBPy})^{3+}$ and (ATBPy) $^{3+}/(\text{ATBPy})^{2+}$. The two single-electron-transfer peaks gradually evolve into one single peak when 2 equiv. HE- β -CD is added. Major change is seen for the peak at -0.87 V , which shows a positive shift and merges with the peak at -0.75 V . The shift in potential should originate from the tunability over the electronic structure when forming the host-guest assembly. Further adding HE- β -CD yields negligible change in CV curves (Fig. S7), which is consistent to the above analysis on the spectra. The differential pulse voltammogram (DPV, Fig. 2b) reveals that the electron transfer number of the single peak is ca. 1.7 in the presence of 2 equiv. HE- β -CD.

The diffusion coefficient (D) of active molecule is derived from the steady-state current collected on a gold disk ultramicroelectrode. The linear sweeping voltammograms (LSVs) in Fig. 2c show that the (ATBPy) $^{4+}$ yields an equal limiting current at different equiv. HE- β -CD, from which the D is calculated as $3.82 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for (ATBPy) $^{4+}$, $3.81 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for (ATBPy) $^{4+}$ with 1 equiv. HE- β -CD, and $3.79 \times$

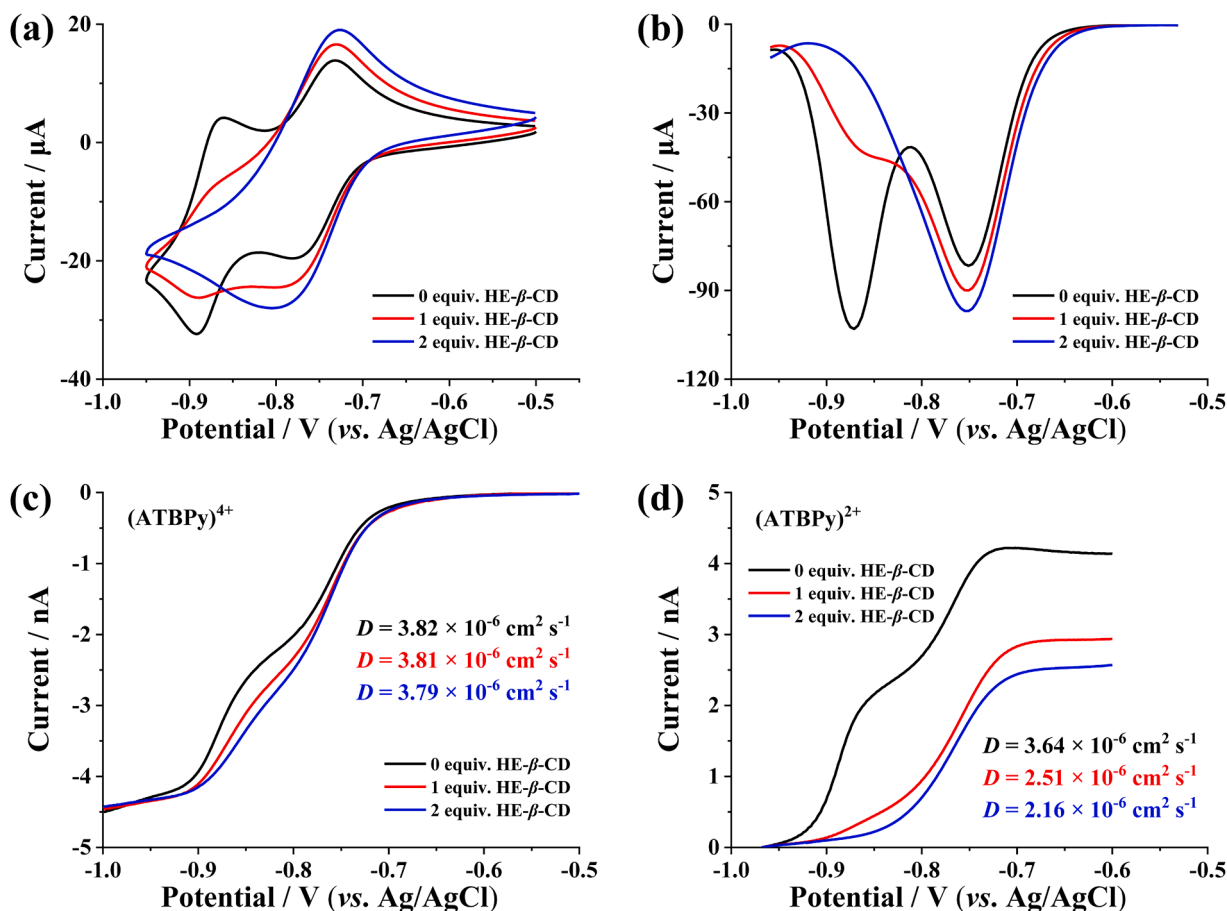


Fig. 2. (a) CVs and (b) DPVs of (ATBPy)Br₄ with different equiv. HE-β-CD; LSVs collected on a gold disk ultramicroelectrode: (c) 1.0 mM (ATBPy)Br₄ and (d) 1.0 mM (ATBPy)Br₂ with different equiv. HE-β-CD.

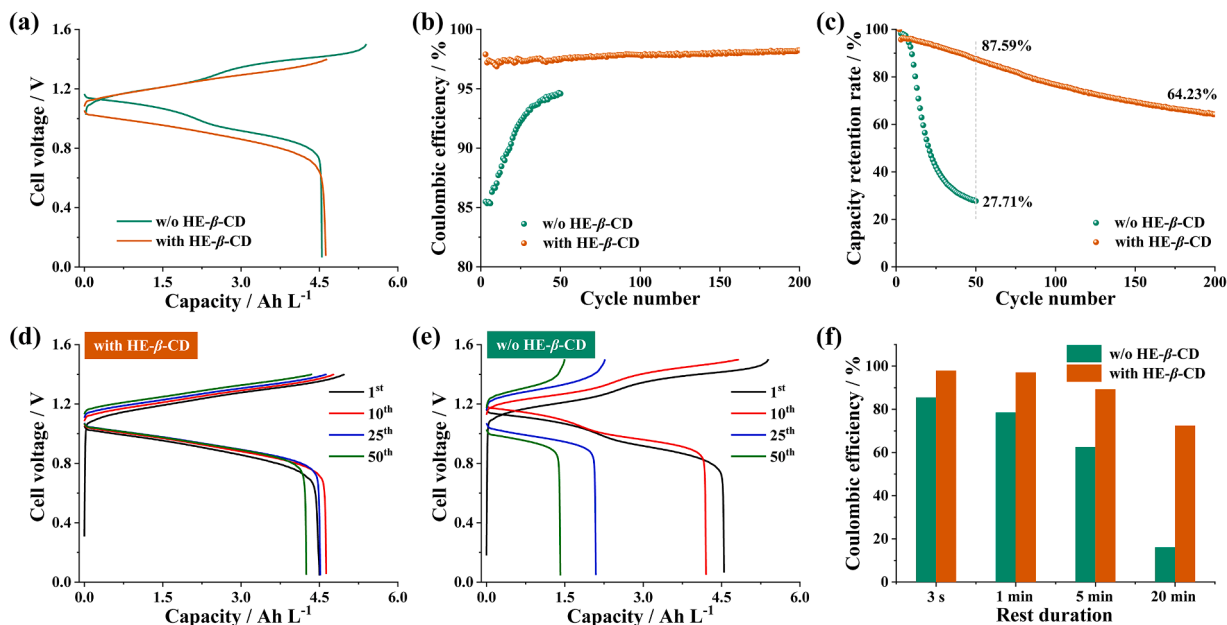


Fig. 3. (a) Galvanostatic charge/discharge profiles at 60 mA cm⁻² of the air-operated flow battery fed with either 0.10 M (ATBPy)Br₄ or 0.10 M (ATBPy)Br₄+0.20 M HE-β-CD; (b) Corresponding CEs with a rest duration of 3 s at the end of charge process; (c) Capacity retention rate of air-operated flow battery; Corresponding charge/discharge profiles of flow battery during 50 cycles: (d) with 2 equiv. HE-β-CD and (e) without HE-β-CD; (f) CEs with different rest durations.

$10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for (ATBPy) $^{4+}$ with 2 equiv. HE- β -CD. This result is unsurprising as the oxidation state of (ATBPy) $^{4+}$ does not form a host-guest complex with HE- β -CD. In comparison, the limiting current of the reduced-state (ATBPy) $^{2+}$ is highly dependent on the amount of HE- β -CD, as seen in Fig. 2d. The D of (ATBPy) $^{2+}$ is calculated as $3.64 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which is decreased by 40 % upon adding 2 equiv. HE- β -CD. Such a remarkable decrease is understandable due to the formation of assembly complex between (ATBPy) $^{2+}$ and HE- β -CD. It is acknowledged that the relationship between the diffusion coefficient and the apparent molecular weight (M) can be expressed by Stokes-Einstein equation [35]. Previous work revealed that the relationship between D and M for the pyridinium-based molecules is as follows [14].

$$\lg D = -0.58 \lg M - 3.76 \quad (2)$$

In accordance with the D value ($1.69 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, Fig. S8), the apparent molecular weight is ca. 3100, which is close to that of the host-guest complex (ATBPy) $^{2+}$ +2HE- β -CD.

3.3. Air tolerance of flow battery

As demonstration, (ATBPy)Br $_4$ is employed as the anolyte in a flow battery, which is paired with air-tolerant (ferrocenylmethyl)trimethylammonium chloride (FcNCl, Figs. S9–S11) as the catholyte. The battery is tested under a harsh condition to verify the effect of HE- β -CD on the air tolerance of (ATBPy)Br $_4$. As shown in Fig. S12, the assembled flow battery is operated outside the glove box, in which the anolyte is exposed to air through a perforated lid (two circular holes, diameter of 5 mm). Fig. 3a presents the corresponding galvanostatic charge/discharge profiles. Without HE- β -CD, the (ATBPy)Br $_4$ -FcNCl flow battery shows two distinct charge/discharge voltage platforms, which correspond to two single-electron-transfer steps (Fig. S6). The charging capacity of

5.39 Ah L $^{-1}$ is achieved at 60 mA cm $^{-2}$ (anolyte capacity limited), which slightly exceeds the theoretical capacity (5.36 Ah L $^{-1}$). The excessive charging capacity should be attributed to the oxygen reduction reaction mediated by the viologen. And a discharging capacity of 4.54 Ah L $^{-1}$ is achieved, realizing a poor Coulombic efficiency (CE) of 84 %. In comparison, the addition of HE- β -CD yields a higher CE of ca. 100 %, which intuitively indicates an enhanced air-tolerant capability. The improvement should originate from the steric hindrance against the oxygen attack by forming the host-guest assembly between the reduced state of (ATBPy)Br $_2$ and HE- β -CD.

Furthermore, only one single smooth voltage platform is observed for the charge/discharge profiles, which is consistent with the overlapping peaks found in CVs (Fig. 2a). Fig. 3b presents the CE of the flow battery during a 200-cycle test. With HE- β -CD, a stable CE of ~98 % is achieved and the flow battery delivers a superior cyclability (Fig. 3c and d). Without HE- β -CD, the capacity yields a drastic decay and drops to 27.71 % in the first 50 cycles (Fig. 3c and e). It is noted that the CE shows a continuous increase during the 50 test cycles when operated without the HE- β -CD (Fig. 3b). It has been reported that the oxygen reduction reaction in the anolyte results in the catholyte's capacity loss [16], which in turn limits the battery's capacity. As such, the charge/discharge time will be shortened as the battery cycling test continues, decreasing the reaction time with air and, thus, increasing the CE. As mentioned above, the capacity fading should be attributed to the oxidation of the reduced-state specie of (ATBPy)Br $_2$ by oxygen in air. The fading effect is further exaggerated by setting rest durations after the battery charging, during which the reduced state of (ATBPy)Br $_2$ is exposed to air (Fig. S13). Fig. 3f shows that the CE continuously decreases as the rest duration increases from 3 s to 20 min, and the introduction of HE- β -CD can effectively lessen the decay rate (84 % versus 27 % @20 min).

A simple packaging of the flow battery is applied to simulate the

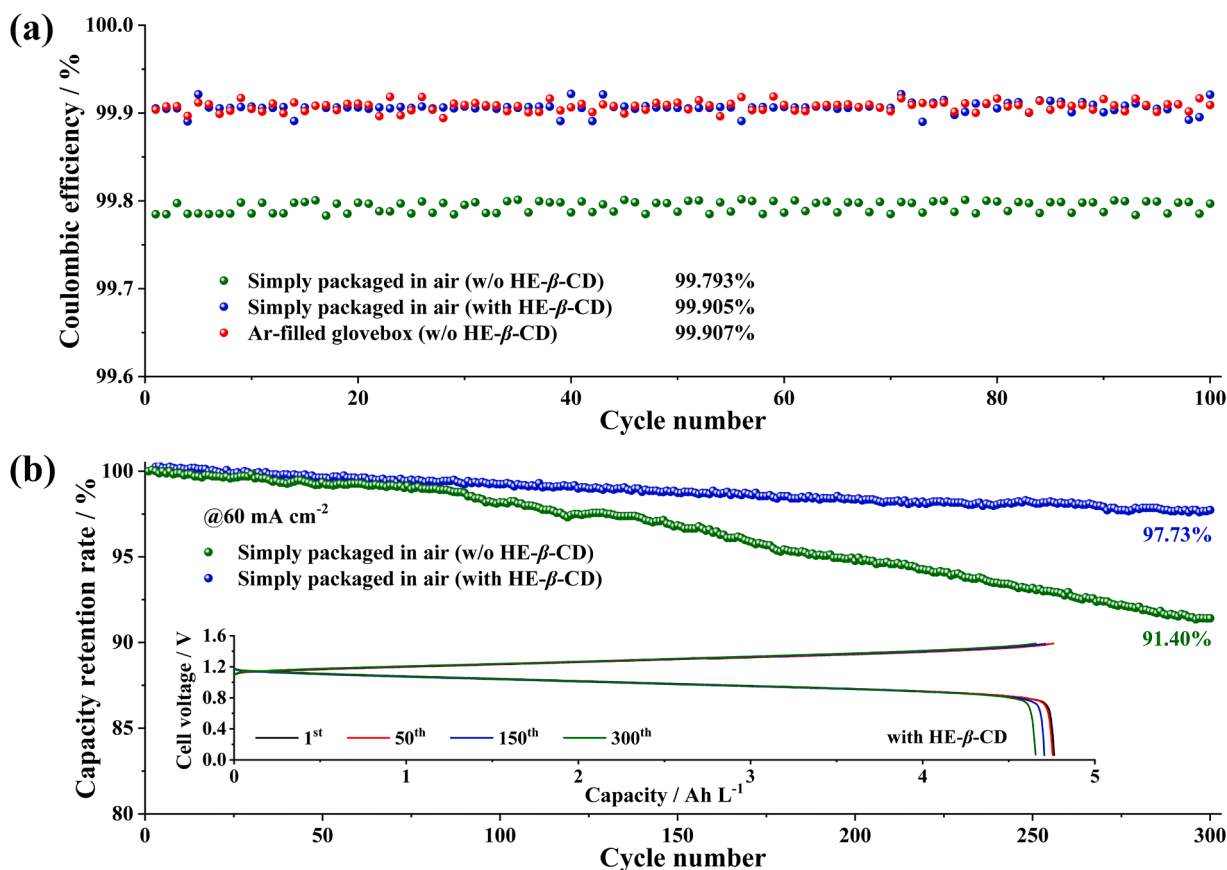


Fig. 4. (a) CEs of the flow battery; (b) Cycling performances of the flow battery (inset: charge/discharge profiles). (Anolyte: 0.10 M (ATBPy)Br $_4$ or 0.10 M (ATBPy)Br $_4$ +0.10 M HE- β -CD; Catholyte: 0.10 M FcNCl).

practical application in air. Fig. 4a shows that the flow battery displays an average CE of 99.793 % during 100 cycles in the absence of HE- β -CD, indicating that the packaging is essential and effective to exclude oxygen. Further adding equal equivalent HE- β -CD can significantly improve the CE to 99.905 %, which is comparable to that operated in an Ar-filled glovebox (99.907 %). As shown in Figs. 4b and S14, a 300-cycle test reveals that at 60 mA cm⁻², the capacity retention is 97.73 % with HE- β -CD and 91.40 % without HE- β -CD, fully demonstrating the validity of the kinetics-based stabilization strategy. It is, however, noted that the operation concentration of the electrolyte is bottlenecked by the solubility of the host molecule (0.40 M for HE- β -CD). Further work includes but is not limited to: (1) increasing the solubility of the host, (2) exploring new molecule engineering strategy, such as introducing oxygen-blocking steric group.

4. Conclusions

In summary, a facile thermodynamic regulation strategy of solution is developed to improve the oxygen tolerance of viologen-based flow battery. The study suggests that the reduced viologen molecule is assembled by HE- β -CD through a hydrophobic interaction to form host-guest complex, in which the HE- β -CD can act as protective screen to protect the viologen against the oxygen attack, thereby improving the air stability of anolyte kinetically. The flow battery achieves stable operation in air environment, showing a high Coulombic efficiency of ~99.9 % and cycling performance (capacity retention rate of 97.73 % over 300 cycles). This work demonstrates an air-operated viologen-based flow battery and provides an efficient route for practical application of AORFB.

CRedit authorship contribution statement

Mingbao Huang: Investigation, Methodology, Data curation, Writing – original draft. **Wenjin Li:** Methodology, Data curation. **Dehan Lin:** Validation. **Kai Wan:** Data curation. **Zhiyong Fu:** Resources, Supervision. **Zhipeng Xiang:** Writing – review & editing. **Zhenxing Liang:** Conceptualization, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was jointly supported by the National Natural Science Foundation of China (22325802, U22A20417, 92372106, 22178126, 22108085), Science and Technology Program of Guangzhou (2023B03J1281), the State Key Laboratory of Pulp and Paper Engineering (2023ZD03), and China Postdoctoral Science Foundation (2023T160223).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ensm.2024.103267.

References

- [1] Y.X. Yao, J.F. Lei, Y. Shi, F. Ai, Y.C. Lu, Assessment methods and performance metrics for redox flow batteries, *Nat. Energy* 6 (2021) 582–588, <https://doi.org/10.1038/s41560-020-00772-8>.
- [2] Z.M. Zhao, X.H. Liu, M.Q. Zhang, L.Y. Zhang, C.K. Zhang, X.F. Li, G.H. Yu, Development of flow battery technologies using the principles of sustainable chemistry, *Chem. Soc. Rev.* 52 (2023) 6031–6074, <https://doi.org/10.1039/d2cs00765g>.
- [3] M.H. Yang, Z.Z. Xu, W.Z. Xiang, H. Xu, M. Ding, L.Y. Li, A. Tang, R.H. Gao, G. M. Zhou, C.K. Jia, High performance and long cycle life neutral zinc-iron flow batteries enabled by zinc-bromide complexation, *Energy Storage Mater.* 44 (2022) 433–440, <https://doi.org/10.1016/j.ensm.2021.10.043>.
- [4] W.Z. Xiang, M.H. Yang, M. Ding, X.X. Chen, J.L. Liu, G.M. Zhou, C.K. Jia, G.I. N. Waterhouse, Alkaline Zn-Mn aqueous flow batteries with ultrahigh voltage and energy density, *Energy Storage Mater* 61 (2023) 102894, <https://doi.org/10.1016/j.ensm.2023.102894>.
- [5] M. Ding, H. Fu, X.C. Lou, M.R. He, B. Chen, Z.Y. Han, S.Q. Chu, B. Lu, G.M. Zhou, C. K. Jia, A stable and energy-dense polysulfide/permanenate flow battery, *ACS Nano* 17 (2023) 16252–16263, <https://doi.org/10.1021/acsnano.3c06273>.
- [6] Y. Xu, C.X. Xie, X.F. Li, Bromine-graphite intercalation enabled two-electron transfer for a bromine-based flow battery, *Trans. Tianjin Univ.* 28 (2022) 186–192, <https://doi.org/10.1007/s12209-022-00327-w>.
- [7] Y. Jing, E.W.B. Zhao, M.A. Goulet, M. Bahari, E.M. Fell, S. Jin, A. Davoodi, E. Jönsson, M. Wu, C.P. Grey, R.G. Gordon, M.J. Aziz, In situ electrochemical recombination of decomposed redox-active species in aqueous organic flow batteries, *Nat. Chem.* 14 (2022) 1103–1109, <https://doi.org/10.1038/s41557-022-00967-4>.
- [8] A. Hollas, X.L. Wei, V. Murugesan, Z.M. Nie, B. Li, D. Reed, J. Liu, V. Sprenkle, W. Wang, A biomimetic high-capacity phenazine-based anolyte for aqueous organic redox flow batteries, *Nat. Energy* 3 (2018) 508–514, <https://doi.org/10.1038/s41560-018-0167-3>.
- [9] T. Janoschka, N. Martin, U. Martin, C. Friebe, S. Morgenstern, H. Hiller, M. D. Hager, U.S. Schubert, An aqueous, polymer-based redox-flow battery using non-corrosive, safe and low-cost materials, *Nature* 527 (2015) 78–81, <https://doi.org/10.1038/nature15746>.
- [10] J.H. Huang, S.Z. Hu, X.Z. Yuan, Z.P. Xiang, M.B. Huang, K. Wan, J.H. Piao, Z.Y. Fu, Z.X. Liang, Radical stabilization of a tripyridinium-triazine molecule enables reversible storage of multiple electrons, *Angew. Chem. Int. Ed.* 60 (2021) 20921–20925, <https://doi.org/10.1002/anie.202107216>.
- [11] S.Z. Hu, L.W. Wang, X.Z. Yuan, Z.P. Xiang, M.B. Huang, P. Luo, Y.F. Liu, Z.Y. Fu, Z. X. Liang, Viologen-decorated TEMPO for neutral aqueous organic redox flow batteries, *Energy Mater. Adv.* 2021 (2021) 9795237, <https://doi.org/10.34133/2021/9795237>.
- [12] T. Janoschka, N. Martin, M.D. Hager, U.S. Schubert, An aqueous redox-flow battery with high capacity and power: the TEMPTMA/MV system, *Angew. Chem. Int. Ed.* 55 (2016) 14427–14430, <https://doi.org/10.1002/anie.201606472>.
- [13] S.Z. Hu, T.Y. Li, M.B. Huang, J.H. Huang, W.J. Li, L.W. Wang, Z.Q. Chen, Z.Y. Fu, X.F. Li, Z.X. Liang, Phenylene-bridged bispyridinium with high capacity and stability for aqueous flow batteries, *Adv. Mater.* 33 (2021) 2005839, <https://doi.org/10.1002/adma.202005839>.
- [14] Z.P. Xiang, W.J. Li, K. Wan, Z.Y. Fu, Z.X. Liang, Aggregation of electrochemically active conjugated organic molecules and its impact on aqueous organic redox flow batteries, *Angew. Chem. Int. Ed.* 62 (2023) e202214601, <https://doi.org/10.1002/anie.202214601>.
- [15] Y.H. Zhang, F. Li, T.Y. Li, M.Q. Zhang, Z.Z. Yuan, G.J. Hou, J. Fu, C.K. Zhang, X. F. Li, Insights into an air-stable methylene blue catholyte towards kW-scale practical aqueous organic flow batteries, *Energy Environ. Sci.* 16 (2023) 231–240, <https://doi.org/10.1039/d2ee03051a>.
- [16] T.Y. Kong, J. Liu, X. Zhou, J. Xu, Y.H. Xie, J.W. Chen, X.F. Li, Y.G. Wang, Stable operation of aqueous organic redox flow batteries in air atmosphere, *Angew. Chem. Int. Ed.* 62 (2023) e202214819, <https://doi.org/10.1002/anie.202214819>.
- [17] Q.Q. Lin, Q. Li, C. Batchelor-McAuley, R.G. Compton, Use of 'split waves' for the measurement of electrocatalytic kinetics: methyl viologen mediated oxygen reduction on a boron-doped diamond electrode, *Phys. Chem. Chem. Phys.* 15 (2013) 7760–7767, <https://doi.org/10.1039/c3cp50873k>.
- [18] C.L. Bird, A.T. Kuhn, Electrochemistry of the viologens, *Chem. Soc. Rev.* 10 (1981) 49–82, <https://doi.org/10.1039/cs9811000049>.
- [19] E.S. Beh, D. De Porcellinis, R.L. Gracia, K.T. Xia, R.G. Gordon, M.J. Aziz, A neutral pH aqueous organic-organometallic redox flow battery with extremely high capacity retention, *ACS Energy Lett* 2 (2017) 639–644, <https://doi.org/10.1021/acsenenergylett.7b00019>.
- [20] B.H. Tang, J.T. Zhao, J.F. Xu, X. Zhang, Tuning the stability of organic radicals: from covalent approaches to non-covalent approaches, *Chem. Sci.* 11 (2020) 1192–1204, <https://doi.org/10.1039/c9sc06143f>.
- [21] M. Berville, J. Richard, M. Stolar, S. Choua, N.Le Breton, C. Gourlaouen, C. Boudon, L. Ruhlmann, T. Baumgartner, J.A. Wytko, J. Weiss, A highly stable organic radical cation, *Org. Lett.* 20 (2018) 8004–8008, <https://doi.org/10.1021/acs.orglett.8b03579>.
- [22] K. Cai, H.C. Mao, W.G. Liu, Y.Y. Qiu, Y. Shi, L. Zhang, D.K. Shen, H.L. Chen, Y. Jiao, H. Wu, Z.C. Liu, Y.N. Feng, C.L. Stern, M.R. Wasielewski, W.A. Goddard, J. F. Stoddart, Highly stable organic bisradicals protected by mechanical bonds, *J. Am. Chem. Soc.* 142 (2020) 7190–7197, <https://doi.org/10.1021/jacs.0c01989>.
- [23] A. Stergiou, J. Rio, J.H. Griwatz, D. Arcon, H.A. Wegner, C.P. Ewels, N. Tagmatarchis, A long-lived azafullerenyl radical stabilized by supramolecular shielding with a [10]cycloparaphenylene, *Angew. Chem. Int. Ed.* 58 (2019) 17745–17750, <https://doi.org/10.1002/anie.201909126>.
- [24] L. Liu, Y.X. Yao, Z.Y. Wang, Y.C. Lu, Viologen radical stabilization by molecular spectrators for aqueous organic redox flow batteries, *Nano Energy* 84 (2021) 105897, <https://doi.org/10.1016/j.nanoen.2021.105897>.
- [25] Y.F. Liu, X.Z. Yuan, M.B. Huang, Z.P. Xiang, S.Z. Hu, Z.Y. Fu, X.H. Guo, Z.X. Liang, Redox-modulated host-guest complex realizing stable two-electron storage viologen for flow battery, *Ind. Eng. Chem. Res.* 61 (2022) 14508–14514, <https://doi.org/10.1021/acs.iecr.2c02272>.

- [26] W.J. Li, S.W. Liao, Z.P. Xiang, M.B. Huang, Z.Y. Fu, L.B. Li, Z.X. Liang, Thermodynamic regulation over nano-heterogeneous structure of electrolyte solution to improve stability of flow batteries, *Chem. Eng. Sci.* 270 (2023), <https://doi.org/10.1016/j.ces.2023.118534>.
- [27] J.A. McCune, M.F. Kuehnle, E. Reisner, O.A. Scherman, Stimulus-mediated ultrastable radical formation, *Chem* 6 (2020) 1819–1830, <https://doi.org/10.1016/j.chempr.2020.05.005>.
- [28] H. Fan, K. Liu, X.D. Zhang, Y.P. Di, P. Liu, J.Q. Li, B. Hu, H.B. Li, M. Ravivarma, J. X. Song, Spatial structure regulation towards armor-clad five-membered pyrroline nitroxides catholyte for long-life aqueous organic redox flow batteries, *eScience* (2023) 100202, <https://doi.org/10.1016/j.esci.2023.100202>.
- [29] M.B. Huang, S.Z. Hu, X.Z. Yuan, J.H. Huang, W.J. Li, Z.P. Xiang, Z.Y. Fu, Z. X. Liang, Five-membered-heterocycle bridged viologen with high voltage and superior stability for flow battery, *Adv. Funct. Mater.* 32 (2022) 2111744, <https://doi.org/10.1002/adfm.202111744>.
- [30] W.S. Jeon, K. Moon, S.H. Park, H. Chun, Y.H. Ko, J.Y. Lee, E.S. Lee, S. Samal, N. Selvapalam, M.V. Rekharsky, V. Sindelar, D. Sobransingh, Y. Inoue, A.E. Kaifer, K. Kim, Complexation of ferrocene derivatives by the cucurbit[7]uril host: a comparative study of the cucurbituril and cyclodextrin host families, *J. Am. Chem. Soc.* 127 (2005) 12984–12989, <https://doi.org/10.1021/ja052912c>.
- [31] M.H. Chai, A.K. Holley, M. Kruskamp, Encapsulating fluorescein using adipic acid self-assembly on the surface of PPI-3 dendrimer, *Chem. Commun.* (2007) 168–170, <https://doi.org/10.1039/b610018j>.
- [32] H.B. Li, H. Fan, B. Hu, L.L. Hu, G. Chang, J.X. Song, Spatial structure regulation: a rod-shaped viologen enables long lifetime in aqueous redox flow batteries, *Angew. Chem. Int. Ed.* 60 (2021) 26971–26977, <https://doi.org/10.1002/anie.202110010>.
- [33] S. Schlucker, R.K. Singh, B.P. Asthana, J. Popp, W. Kiefer, Hydrogen-bonded pyridine-water complexes studied by density functional theory and raman spectroscopy, *J. Phys. Chem. A* 105 (2001) 9983–9989, <https://doi.org/10.1021/jp0122272>.
- [34] K. Takahashi, T. Nihira, K. Akiyama, Y. Ikegami, E. Fukuyo, Synthesis and characterization of new conjugation-extended viologens involving a central aromatic linking group, *J. Chem. Soc., Chem. Commun.* 8 (1992) 620–622, <https://doi.org/10.1039/C39920000620>.
- [35] D.P. Valencia, F.J. González, Understanding the linear correlation between diffusion coefficient and molecular weight. A model to estimate diffusion coefficients in acetonitrile solutions, *Electrochem. Commun.* 13 (2011) 129–132, <https://doi.org/10.1016/j.elecom.2010.11.032>.